PCDD AND PCDF LEVELS IN BABY FOOD MADE FROM CHICKEN PRODUCED BEFORE AND AFTER 1997 IN THE UNITED STATES

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Introduction

Animal food products are important contributors to the continuing non-occupational exposure of humans to polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF). For example, the United States Environmental Protection Agency (US EPA) and United States Food and Drug Administration (US FDA) discovered μg/Kg levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and other PCDDs[1] in a feed additive called ball clay. The PCDD containing ball clay was used in the production of soybean meal used to make chicken feed, catfish nuggets and cow pellets in the Southern United States during the 1990s. Approximately 1% of animal feed products contained ball clay that significantly affected the PCDD levels in food animals fed the contaminated feeds[1]. The discovery prompted immediate intervention by US FDA, which stopped further distribution of contaminated soybean meal by manufacturers in early June of 1997 in Arkansas[1]. Chicken and catfish producers switched to feed that did not contain ball clay. Subsequent PCDD analysis of chicken eggs and catfish revealed low or non-detectable levels of TCDD[1]. Broiler chickens fed ball clay-containing feed during and prior to 1997 came from two broiler producers with plants located in Arkansas and Oklahoma. Although contaminated ball clay use in feeds had been halted by June 1997; contaminated chicken products may still have been in processed food products already sold to retail outlets in 1996 and 1997. The goals of this investigation were to: (1) measure the impact of ball clay use on PCDD/F levels in chicken containing baby food collected in 1997/98; (2) measure background PCDD/F levels in baby food after ball clay use had ceased and compare these levels with chicken eggs not affected by ball clay: and (3) test for significant differences between the 1997/98 and 1999 TCDD levels in baby food.

Experimental

Study Design and Sample Collection

A representative cross-sectional sampling of baby food products containing chicken is normally included into US FDA's annual Total Diet Study. Each year food from approximately 300 different types of commonly consumed products, including baby foods, is collected during each quarter of the fiscal year (FY, Oct. 1 to Oct 1). Each of the four collections is performed in a different region of the U.S. FDA inspectors collected 3 baby food products containing chicken from two producers (3 of each) each fiscal quarter for the last half of the fiscal year 1997 and the first half of FY 1998. The samples were immediately transported on ice to the Center for Food Safety and Applied Nutrition (CFSAN) for dioxin analysis.

Eleven chicken containing baby foods were selected for dioxin analysis in 1997 from the last half of FY 97 and the first half of FY 98. The samples covered baby food from three processors. Expiration dates for 8 of these fell between October 1998 to September 1999 (Table 1). One sample collected in the last quarter of 1997 had an expiration date of December 1999 and 2 samples collected in the second quarter of 1998 had dates of December 1999 and May 2000.

Sampling of baby food products was resumed in September of 1999. By this time, baby food produced during or prior to 1997 would have been sold or should have been pulled from the shelves as it reached its expiration date. Products were collected from four region of the US, covered three baby food brands, and came from some of the same production plants as in the FY 97/98 collections.

PCDD levels were measured in all samples from 1997, 1998 and 1999. Mean values for TCDD were tested using a Wilcoxon rank sum test. Total toxic equivalence was not tested. TCDD was previously demonstrated to be the major contributor to the dioxin TEQ in ball clay affected food samples[1].

In 1997, FDA inspectors collected a total of 15 egg samples (two per company, except in Oregon) from 8 companies located in 8 states with no known source of contamination and from chickens that were not fed ball clay. The companies were located in California, Ohio, Georgia, New York, Pennsylvania, Oregon, Minnesota and Wisconsin. All egg samples were collected as unshelled eggs (two dozen whole eggs per sample) and shipped by overnight express to the laboratory.

PCDD/Fs Methods

Egg methodology is described elsewhere[2]. Test portions of baby food were analyzed in batches of three with a blank. Forty gram test portions weighed in 500 mL Teflon screw capped bottles were homogenized with 250 mL cyclohexane/dichloromethane and 280 g anhydrous sodium sulfate. Homogenates were fortified with 15 $^{13}C_{12}$ PCDD/F standards before further purification. PCDD/Fs were measured by quadrupole ion storage tandem mass spectrometry (QISTMS)[2]. Non-detects were set to a value equal to one half the limit of detection (LOD).

Table 1. Baby food collection by region, brand, fat percent, expiration and processing plant in 1997.

FY[1] (quarter)	Region	Brand	%fat	Expiration date	Processing Plant
97(3)	Northeast	B	5.6	2/99	P1324
97(3)	Northeast	B	5.6	3/99	P748
97(3)	Northeast	C	2.8	10/98	-*
97(4)	Central	B	5.6	6/99	P10
97(4)	Central	A	9.9	12/99	P3387
97(4)	Central	A	9.9	7/99	P2137
98(1)	Northwest	A	9.9	9/99	P2557
98(1)	Southwest	B	5.6	8/99	P748
98(2)	South Central	A	9.9	12/99	P3387
98(2)	South Central	B	5.6	4/99	P748
98(2)	Southeast	C	2.8	5/00	-*

*Plant not identified
[1]Fiscal year (FY)

Results and Discussion

PCDD/Fs concentrations were measured for 11 samples of baby food made from chickens collected in FY 97/98. These 11 samples represent a cross-section of these food types found in 11 metropolitan regions (Table 1) and contained TCDD concentrations ranging between non-detect (LOD = 0.02 ng/Kg) to 0.28 ng/Kg wet weight. PCDD/Fs measurements of eggs collected in 1997 nationwide from producers that never used ball clay suggested that TCDD as well as most congeners other than HpCDD and OCDD would be not detected (Table 2). TCDD was not detected in any of these egg samples collected in 1997 above 0.02 pg/g wet weight (0.19 pg/g fat).

Table 2. Whole egg PCDD and PCDF mean concentrations and mean LODs pg/g wet weight whole egg for 15 samples (24 eggs per sample) collected in 1997 from California, Ohio, Georgia, New York, Pennsylvania, Oregon, Minnesota and Wisconsin (2 samples from each state except Oregon).

	Mean (+) N=15	Mean LOD
2,3,7,8-TCDD	0.009(1)	0.02
1,2,3,7,8-PeCDD	nd	0.04
1,2,3,4,7,8-HxCDD	nd	0.08
1,2,3,6,7,8-HxCDD	nd	0.09
1,2,3,7,8,9-HxCDD	nd	0.08
1,2,3,4,6,7,8-HpCDD	0.31(13)	0.14
OCDD	1.2(14)	0.2
2,3,7,8-TCDF	0.042(2)	0.04
1,2,3,7,8-PeCDF	0.043(3)	0.05
2,3,4,7,8-PeCDF	0.061(3)	0.046
1,2,3,4,7,8-HxCDF	0.12(1)	0.095
1,2,3,6,7,8-HxCDF	0.081(1)	0.094
2,3,4,6,7,8-HxCDF	NR	NA
1,2,3,7,8,9-HxCDF	nd	0.11
1,2,3,4,6,7,8-HpCDF	0.11(5)	0.098
1,2,3,4,7,8,9-HpCDF	nd	0.1
OCDF	0.12(5)	0.18
TEQ (nd=1/2 LOD)	0.038	

nd= not detected; NR = not reported; NA = not applicable
(+) = number positive

TCDD was detected in 8 of 11 baby food samples from FY 97 and 98, but was not detected in any of the 1999 samples (Table 3). TCDD (LOD = 0.02-0.04 ng/Kg wet weight) was not detect in all the 1999 samples which was consistent with earlier results from eggs (Table 2). Other PCDD/Fs were largely undetectable in samples collected in 1999, unlike some of the background chicken fat

measured in 1997 by Ferrairo et al[3]. This was due in part to the low fat content of processed baby foods[3].

Three baby food samples with the highest TCDD levels were packaged in a single plant in Fort Smith, Arkansas. The mean TCDD concentration in these baby food samples was higher than the 1999 samples, including baby food prepared at this plant and collected in 1999. Elevated levels of TCDD and other dioxin congeners found in the 1997/98 baby food may have originated in part from chickens fed ball clay containing feed.

Chicken fat contaminated with ball clay typically contained larger amounts of 1,2,3,7,8,9-HxCDD than 1,2,3,6,7,8 or 1,2,3,4,7,8-HxCDD[3]. Only one 1997 baby food sample (with very low TCDD) contained detectable levels of 1,2,3,7,8,9-HxCDD, while 1,2,3,6,7,8-HxCDD was detected in half the 1997 samples. Based on the ratio of TCDD to 1,2,3,7,8,9-HxCDD concentrations found in chicken fat contaminated from ball clay[3], the predicted 1,2,3,7,8,9-HxCDD concentration in the baby food with the highest amount of TCDD should have been 3 times the LOD for 1,2,3,7,8,9-HxCDD in that sample. All other baby food samples in which TCDD was detected had predicted concentrations of 1,2,3,7,8,9-HxCDD at or below the LOD.

Table 3. Baby food 2,3,7,8-TCDD levels in ng/Kg fat, means(n) and ranges for all samples and for plant P748 only in 1997/98 and 1999.

	1997/98		1999	
	mean(11)	range	mean(6)	range
All samples[1]	1.3	nd(0.13)[2]-5	(0.21)	(0.15)-(0.28)
Plant P748[1]	2.8 (n=3)	1-5	(0.25) (n=2)	(0.22)-(0.28)

[1]Statistically significant, Wilcoxon rank sum, p-value for all samples, $p<0.005$ and plant P748, $p<0.1$

[2]( ) = ½ the LOD

(1) Hayward, D. G., Nortrup, D., Gardner, A., Clower, M., *Environ. Res.* **1999**, 81, 248-256.
(2) Hayward, D. G., Hooper, K., and Andrzejewski, D., *Anal. Chem.* **1999**, 71(1), 212-220.
(3) Ferrario, J., Byrne, C., Lorber, M., Saunders, P., Leese, W., Dupuy, A., Winters, D., Cleverly, D., Schaum, J, Pinsky, P., Deyrup, C., Ellis, R., Walcott, J., *Organohalogen Compounds* **1997**, 32, 245-251.